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13. ABSTRACT (Maximum 200 words)

The research program demonstrated that the overall nonradiative deexcitation taking place in impurity-doped laser crystals can be broken down into three distinct steps: generation of local mode population due to transition through electronic bottleneck, energy transfer from local into select phonon modes via local-phonon mode coupling and return of the system to thermal equilibrium via interaction of the active phonons with the phonon bath. . The mechanism of the nonradiative decay is investigated for each step using three experimental techniques : resonance Raman scattering for the identification of Cr^{4+} local modes, and up-converted hot luminescence and time resolved Raman scattering for the identification of the phonons involved in the nonradiative decay. The dynamics of the phonon modes involved in the nonradiative relaxation was analyzed using a newly developed theoretical model which provided characteristic relaxation time parameters. This work provided the first step in understanding how to alter and control the flow of nonradiative energy.

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   b. Dana M. Calistru, S. G. Demos, R. R. Alfano, "Direct Observation of second neighbor interactions for Cr^{4+}-doped forsterite by resonance Raman scattering", Appl. Phys. Lett. **68**, 2207 (1996).

   c. S. G. Demos, Dana M. Calistru, R. R. Alfano, "Criterion for selecting phonons and local vibrations involved in the nonradiative relaxation of photoexcited Cr^{4+} ions in forsterite", Appl. Phys. Lett. **68**, 1195 (1996).

   d. V. A. Kremerman, M. Lax, S. G. Demos, Dana M. Calistru, R. R. Alfano, "Nonradiative energy transfer from impurity ion into the host lattice for Cr^{4+}-doped forsterite laser crystal", Phys. Rev. **B56**, 14391 (1997).

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   Ms. Dana M. Calistru - Ph.D., CUNY, September 4, 1997.

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Experimental and theoretical program was undertaken to study and better understand the mechanism of nonradiative relaxation of hot photoexcited ions in crystals. This work relates how energy flows nonradiatively and how to alter it. Our studies suggest that the overall nonradiative transition following the photoexcitation of an impurity ion can be broken down into three steps, as follows :

(1) An electronic transition through an electronic bottleneck generates a large local mode population (impurity associated modes of vibration).

(2) The energy stored for a brief time (~ps) in the local modes is transferred to select phonon modes (lattice host modes of vibration) via harmonic and anharmonic coupling.

(3) The phonon modes "lose" their energy via anharmonic coupling with the phonon bath, and the system returns to thermal equilibrium.

The importance of breaking the overall nonradiative process into well defined steps is to show that different mechanisms are involved. The first step implies the conversion of a large electronic energy into local vibrational energy and depends on the strength of the electron-phonon interactions. In the second step, energy is interchanged between two vibrational subsystems (local and phonon modes) such that only select phonon modes take over the excess energy stored in local modes. We proposed in this research the energy resonance between local and phonon modes as a main criterion determining the coupling between the two vibrational subsystems. This understanding may lead to ways to direct the nonradiative pathway of energy flow.

In order to investigate the three steps of the nonradiative process, three different techniques were used. The selected material under investigation was Cr^{4+}-doped forsterite (Mg_2SiO_4). Each technique, together with relevant results are briefly described in the following sections.

a) Polarized resonance Raman scattering was used to identify the laser ion's (Cr^{4+}) local modes. If the excitation wavelength is tuned in an absorption band of an ion under

investigation, the modes of vibration associated to the ion appear in addition to the host's phonon modes. By comparing a resonance Raman spectrum with an off-resonance spectrum (which contains only phonon modes) the ion's local modes can be identified in terms of energy and symmetry. The mode-locked, frequency doubled output of a Nd:YAG laser was used to pump a Rh-6G dye laser which provided the excitation wavelength (572 nm) corresponding to the $^3A_2 \rightarrow {}^3B_2(^3T_1)$ Cr^{4+} absorption band. Fifteen Cr^{4+} local modes were identified in the first order spectrum [1], as follows (the symmetry is given in *Pnma* crystal notation) : 8 A_g modes at 253, 288, 346, 361, 390, 499, 691 and 765 cm^{-1}, 5 B_{3g} modes at 408, 420, 477, 526 and 742 cm^{-1}, and 2 B_{2g} modes at 468 and 820 cm^{-1}. The on-resonance (572 nm excitation - upper profile) and off-resonance (582 nm excitation - lower profile) totally symmetric (A_g) spectra of Cr:Mg_2SiO_4 obtained at 77K are shown in Fig.1. The off-resonance Raman spectrum contains only phonon modes and a very weak local mode at 765 cm^{-1}, which disappears under 585 nm excitation. Cr^{4+} local modes are boxed.
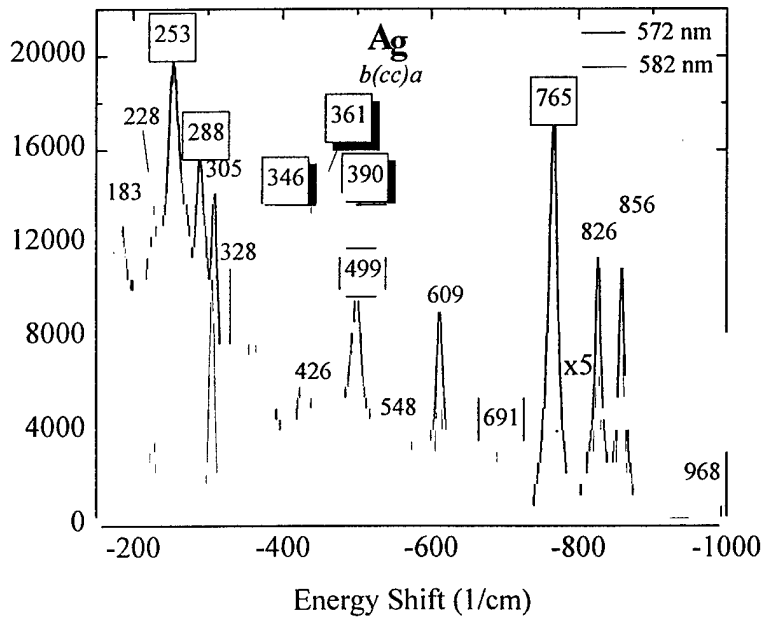

Figure 1. First order A_g resonance Stokes Raman spectra (boxed modes) for Cr^{4+}:Mg_2SiO_4 obtained under resonant 572 nm (thick line) and off-resonance 582 nm (thin line) excitation at 77K. The scattering configuration is *b(cc)a*. Local modes are boxed. Highlighted local modes were not observed in room temperature spectra.

b) Up-converted hot luminescence measurements [2] take advantage of a two-step excitation process. If the excitation energy is E_{ex}, the first step of the process photoexcites the ions under investigation on an upper electronic level situated at E_{ex}. The ions then deexcite to the long lived (μs) metastable level of energy E_{ML}. If a second photon of energy E_{ex} is absorbed before the metastable level is depleted, the ion will be photoexcited at an energy $E_{ML}+E_{ex}$. Emission from this high energy state, which is situated well above the fluorescence region from the metastable, identifies the select phonons involved in the initial steps of the nonradiative deexcitation as consecutive peaks in the emission profile. Up-converted hot luminescence measurements performed in $Cr:Mg_2SiO_4$ demonstrate that only select phonon modes at $\omega_1 \approx 225$ cm^{-1}, $\omega_2 \approx 335$ cm^{-1} and $\omega_3 \approx 370$ cm^{-1}, participate in the nonradiative relaxation process of the photoexcited laser impurity ion.

The comparison between the spectrum of the above mentioned active phonon modes (participating in the nonradiative relaxation process) and the local mode spectrum measured by resonance Raman scattering indicates that a criterion which selects the modes participating in the nonradiative decay is the local-phonon energy resonance [3]. Different types of coupling as determined by the local-phonon energy mismatch are schematically depicted in Fig. 2.

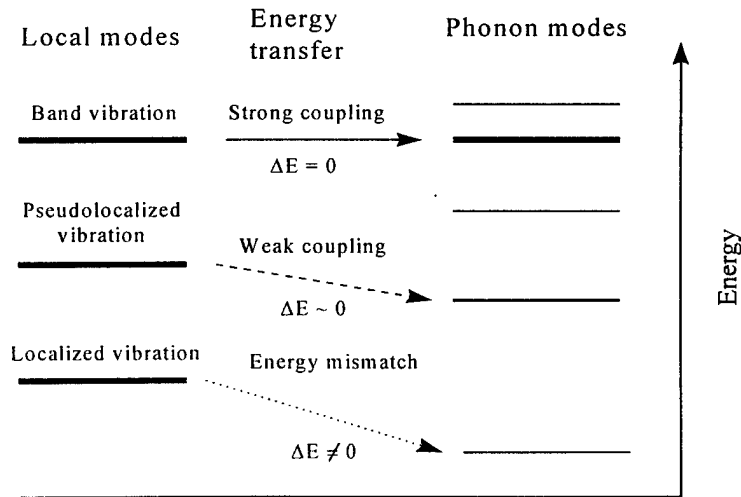| Local modes	Energy transfer	Phonon modes
Band vibration	Strong coupling $\Delta E = 0$	
Pseudolocalized vibration	Weak coupling $\Delta E \sim 0$	
Localized vibration	Energy mismatch $\Delta E \neq 0$	

Energy

Figure 2 Schematic picture of different types of coupling between local modes and phonon modes, based on the energy resonance criterion.

c) Pump-probe time resolved Raman scattering experiments [4] have measured the dynamics of the phonon modes involved in the nonradiative deexcitation. In order to determine the characteristic parameters of the nonradiative decay a theoretical model was developed [5]. This model takes into account the three previously mentioned distinct steps of a nonradiative process (1) - 3)) and provides a system of equations describing the nonradiative relaxation of a phonon mode due to the relaxation of the photoexcited ion as :

$$\frac{d\overline{N}(t)}{dt} = \gamma[-\overline{N}(t) + \overline{n}(\varepsilon_c, t)] + ke^{-\Gamma t}$$

$$\frac{d\overline{n}(\varepsilon_c, t)}{dt} = \mu[-\overline{n}(\varepsilon_c, t) + \overline{N}(t)] + \zeta(\varepsilon_c)[-\overline{n}(\varepsilon_c, t) + n_0(\varepsilon_c)].$$

(1)

where $\overline{N}(t)$ is the nonequilibrium local mode population, $\overline{n}(t)$ is the nonequilibrium phonon population. The parameters μ^{-1} (= γ^{-1}) which represent the characteristic local mode lifetime, Γ^{-1} which is the electronic transition lifetime and ζ^{-1} which is the characteristic phonon mode lifetime were determined by fitting the experimentally measured dynamics of phonon modes during the nonradiative relaxation of Cr^{4+} ions as follows : electronic relaxation lifetime $\Gamma^{-1} \sim 3$ ps, time for the energy transfer from local modes to resonant crystal vibrations $\gamma^{-1} \sim 8$ ps, and time needed to establish thermal equilibrium among lattice vibrations for forsterite, $\zeta^{-1} \sim 4$ ps.

This research has opened a new direction towards understanding how to study the mechanisms responsible for nonradiative processes and has provided salient information regarding the individual steps and the specific mechanisms at different stages of the nonradiative decay. Future research will be carried out in Cr^{4+}-doped forsterite analogs (such as $Cr^{4+}:Ca_2GeO_4$ - Cunyite,...) providing information on the underlying physical parameters which may be responsible for controlling the direction of nonradiative decay and energy flow in impurity doped solid state crystals.

Bibliography

1. Dana M. Calistru, S. G. Demos and R. R. Alfano, Phys. Rev. **B52**, 15253 (1995).

2. S. G. Demos, Y. Takiguchi, and R. R. Alfano, Optics Lett. **18**, 522 (1993).

3. S. G. Demos, Dana M. Calistru, R. R. Alfano, Appl. Phys. Lett. **68**, 1195 (1996).

4. S. G. Demos and R. R. Alfano, Phys. Rev. B **51**, 687 (1995).

5. V. A. Kremerman, M. Lax, S. G. Demos, Dana M. Calistru, R. R. Alfano, Phys. Rev. **B56**, 14391 (1997).